

Rec'd PCT/PTO 06 MAY 2005  
PCT/CA 03/016964  
05 DECEMBER 2003 05.12.03

REC'D 21 JAN 2004

WIPO PCT

PA 1089542

# THE UNITED STATES OF AMERICA

**TO ALL TO WHOM THESE PRESENTS SHALL COME:**

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

November 05, 2003

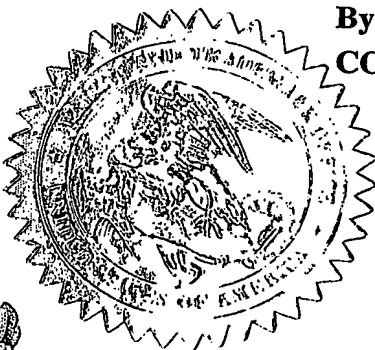
THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE UNDER 35 USC 111.

APPLICATION NUMBER: 60/424,699

FILING DATE: November 08, 2002

**PRIORITY DOCUMENT**  
SUBMITTED OR TRANSMITTED IN  
COMPLIANCE WITH  
RULE 17.1(a) OR (b)

By Authority of the  
COMMISSIONER OF PATENTS AND TRADEMARKS



*P. Swain*  
P. SWAIN  
Certifying Officer

BUSINESS RELATIONS:

# PROVISIONAL APPLICATION COVER SHEET

A/P Ra

This is a request for filing a **PROVISIONAL APPLICATION** under 37 CFR 1.53(b)(2)

Docket Number		11437-1		Type a Plus Sign (+) inside this Box ->		+	
INVENTOR(S)/APPLICANT(S)							
LAST NAME		FIRST NAME		Middle Initial		RESIDENCE (CITY AND EITHER STATE OR FOREIGN COUNTRY)	
LI		Yuning				701-240 Brittany Drive, Ottawa, Ontario, K1K 0R7, Canada	
DING		Jianfu				699 La Vérendrye Drive, Apt. 10, Gloucester, Ontario, K1J 7X5, Canada	
TITLE OF THE INVENTION (280 CHARACTERS MAX.)							
Fabrication Of Multi-Layered Organic Devices Using Crosslinkable Functional Materials Containing Organoboronic Acid Groups							
CORRESPONDENCE ADDRESS							
J. Wayne Anderson National Research Council of Canada Intellectual Property Services Office, EG-10, Bldg. M-58 Montreal Road, Ottawa, Ontario, Canada K1A 0R6							
STATE		Ontario		ZIP CODE		K1A 0R6	
				COUNTRY		Canada	
ENCLOSED APPLICATION PARTS (Check all that Apply)							
X		Specification		Number of pages		13	
						Small Entity Statement	
X		Drawing(s)		Number of Sheets		Other (specify)	
METHOD OF PAYMENT (Check One)							
		A check or money order is enclosed to cover the Provisional filing fees				Provisional Filing Fee Amount (\$)	
X		The Commissioner is hereby authorized to charge filing fees and any deficiency in the filing fees and credit to our <u>Mastercard Account</u> Form PTO-2038 is attached				\$ 160.00	
X		We hereby authorize you to deduct any deficiency of the fee stated above or credit to this amount to our <u>Deposit Account</u> 14-0429.					

The invention was made by an agency of the United States Government or under contract with an agency of the United States Government. ☒ No

No

Date:

Respectfully submitted,

J. Wayne Anderson  
Patent Agent for Applicant  
Regn No. 28,158

Enclosures  
:ech

X Additional inventors are being named on separately numbered sheets attached hereto.

## PROVISIONAL APPLICATION FILING ONLY

Docket Number		11437-1	Type a Plus Sign (+) inside this Box -->	+
INVENTOR(S)/APPLICANT(S)				
LAST NAME	FIRST NAME	Middle Initial	RESIDENCE (CITY AND EITHER STATE OR FOREIGN COUNTRY)	
DAY	Michael		994 Buckskin Way, Orleans, Ontario, K1C 2Y6, Canada	
TAO	Ye		1671, Place des Ravins, Ottawa, Ontario, K1C 6H5, Canada	
D'IORIO	Marie		1954 Mulberry Crescent, Gloucester, Ontario, K1J 8J9, Canada	

## BACKGROUND OF THE INVENTION

20

25

•

Since a multi-layered device structure is a critical step in fabricating highly efficient polymer based devices, much research effort has been devoted to this area.

5 Researchers have developed different strategies to fabricate multi-layered PLED structures using 1) polymer materials of very different solubility, 2) plastic lamination processes or cross-linkable polymer layers, as well as 3) vapor deposition polymerization to avoid the use of solvents. Bernius et al.[1] reported the use of fluorene triphenylamine copolymers with carboxylic acid substituents for the hole-

10 transport layer, as these are soluble in polar solvents like DMF, but practically insoluble in aromatic hydrocarbons such as toluene and xylene. An electron-transport and light-emitting fluorene polymer layer was then spin-coated on top of this layer using a xylene solution. A double layer structure with sharp polymer-polymer

---

interface was successfully produced using this method. Hay et al. have developed a

15 new series of arylamine-based hole-transport polymer[2,3] that can only be dissolved in some organic solvents such as chloroform, for use in double layer PLEDs fabrication. By using electron transport polymers that are soluble in toluene, double layered polymer blue light emitting devices have been successfully fabricated[4]. Yang and his co-workers[5] recently reported a low temperature lamination method

20 using a 'template activated surface process' to fabricate high performance double layer blue and red light-emitting PLEDs at a temperature much lower than the  $T_g$  of the polymers used in their devices. As an alternative approach for making multi-layered polymer devices, Murata[9] recently reported a two-layered polymer light-emitting device prepared by a vapor deposition polymerization process, which has the

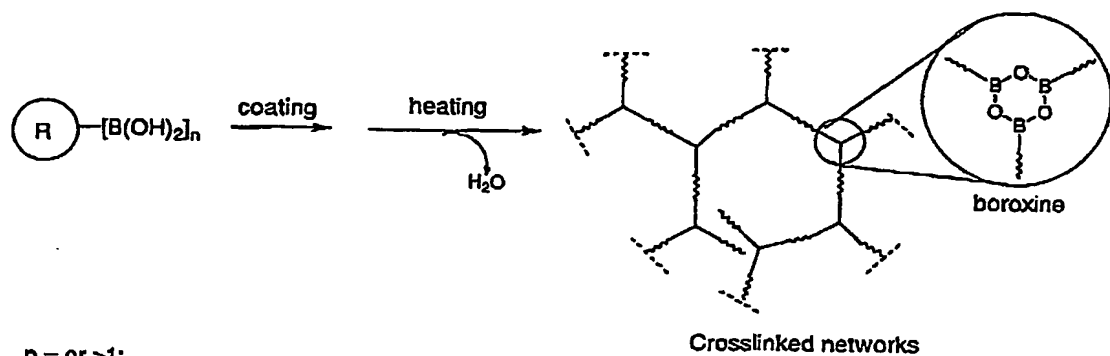
25 advantage of solvent-free fabrication environment, good thin film uniformity, and

minimum contamination. But the fabrication cost could be a problem, and the vapor phase polycondensation reaction used in his experiment might be difficult to apply to other polymer systems. The invention of cross-linkable oligo- and poly(dialkylfluorene)s possessing styryl end groups [6-8] certainly opened a door for multi-layer PLED fabrication using solution processable and thermally cross-linkable polymeric or oligomeric materials.

However, crosslinkable polymer materials used require the attachment of crosslinkable functionalities to the polymers, that usually adds the tediousness to the synthetic procedure and often encounter the difficulties in finding out the optimum content of crosslinkers and crosslinking conditions. In addition, in many cases thermal (at high temperatures) or photo initiators are necessary for the crosslinking reactions to occur. Not only the very reactive radicals destroy the materials' chemical structure to form defects (which are detrimental to the device's performance and lifetime), but also the initiator residues contaminate the materials.

It is an objective of the present invention to overcome the above mentioned disadvantages.

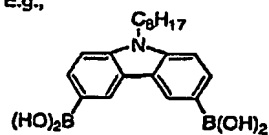
It is known that organoboronic acids undergo self-condensation (dehydration) reactions under vacuum or/and heating to form trialkyl-(or triaryl-) boroxine structure.4-6 Therefore, from di- or multi-organoboronic acids, cross-linked networks would be expected.6 If the organic moiety of the boronic acids is a functional group (see Figure 1) such as, an electron-withdrawing, electron-donating, or light-emitting unit, then these network materials could be used as charge-transporting or light-emitting layers in LED's or other devices.



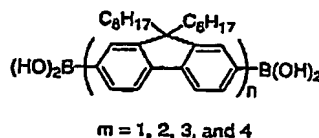
5

$n = \text{or} > 1$ ;  
 $R = \text{organic or organometallic complex moiety including oligomer and polymer.}$

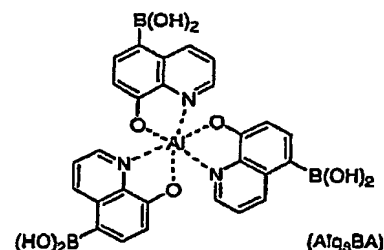
E.g.,



(CzBA)



(FnBA)



(Alq3BA)

Figure 1

## 10 SUMMARY OF THE INVENTION

As described in Figure 1, we have attached organoboronic acids to variety of molecules with very different functions, such as hole transporting, electron transporting and light emitting. Due to the self-condensation process, the molecules will be cross-linked via the organoboronic groups by the heating process, therefore these modified

15 materials can be used either as individual layers in multi-layer devices, or be used to produce new composite materials by simply mixing molecules with different functionalities followed by cross-linking in a single layer, e.g. cross-linking molecules with hole-transport moiety and electron transport moiety in right ratio will render the composite material better charge transport properties.

20 In this invention, we demonstrated the use of organoboronic acids as cross-linking end groups (or side groups) to immobilize the functional materials in a thin film for

tion, we expect this film processing technique (using organoboronic acid groups as end caps) can be applied to the fabrication of photovoltaic cells, photonic multi-layer structures, and any other organic electronic/optical devices which require a multi-layered structure.

In this invention (see Figure 3), the multi-layer structure consists of a glass substrate or any transparent substrate. The second layer is a transparent electrode, indium tin oxide (ITO) anode, as an example. The third layer is a hole transporting layer, CzBA, as an example, then an emissive layer, F3 BA, as an example, was used in the device, which also functions as a electron-transporting layer, and finally followed by a second electrode, Mg:Ag cathode in this case .

**Procedure (double-layer device as an example):**

1. ITO coated glass substrates were patterned using conventional photolithography and wet chemical etching. The pixel size is 5mm x 5mm. Thin films and double layer structure were prepared as described below.
2. The CzBA thin films were spin-coated onto plasma treated ITO from a THF solution (20mg CzBA/ml) at 1500 rpm for 50 sec. The CzBA films prepared under this condition are about 110-120 nm thick. Films were heated in a vacuum oven at 130 °C for two hours to complete the cross-linking reaction (the film could be crosslinked at room temperature-130 °C according the chemical



property of this boronic acid). No thickness change was observed after the heat treatment (within 10% of accuracy).

3. Then the F<sub>3</sub>BA layer was spin-coated on the top of cross-linked CzBA layer from a THF solution (20mg F<sub>3</sub>BA/ml), at 1500rpm for 50 sec. The F<sub>3</sub>BA films prepared under this condition are about 120-130 nm thick, which were measured on separated ITO-glass substrates. Films were heated in a vacuum oven at 130 °C for two hours to complete the cross-linking reaction. The total thickness of the resulted double layer structure was 250 nm, that is equal to the sum of the thickness of individual CzBA and F<sub>3</sub>BA layers prepared on separated ITO-glass substrates. This indicates strongly that the CzBA layer sustains during the coating of the F<sub>3</sub>BA layer.

4. Mg:Ag (10:1) alloy electrode was prepared under high vacuum by co-evaporating Mg and Ag metals.

## RESULTS AND DISCUSSION

### Stability of photoluminescence upon heating:

Upon heating in a vacuum oven at 130 °C for two hours, the CzBA thin films only show slight red shifts in the UV-vis and fluorescence spectra (Figure 2).

Similar results were obtained for F<sub>3</sub>BA films upon heating (Figure 3). Another important feature in the FL spectra is that the intensity did not decrease after a thermal treatment in vacuum. These results indicated that the cross-linking process used here did not cause substantial changes in the optical properties of this light-emitting material



For the comparison, three device structures were used as follows (Figure 4):

(a) (b) (c)

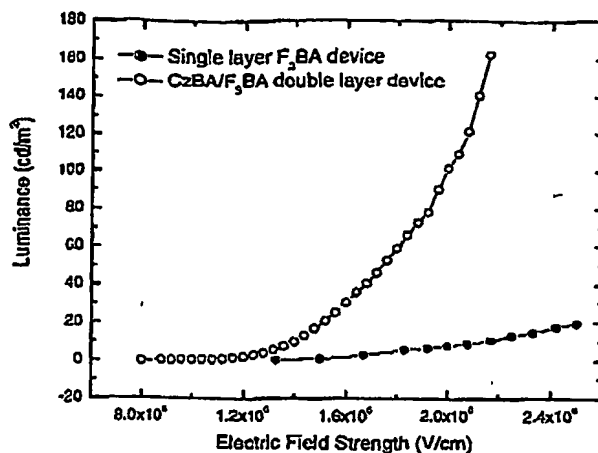


Figure 6

3. At the same electric current density, the double layer structure device emits more intense light, i. e. the device efficiency is much higher, than the single layer structure device (Figure 7).

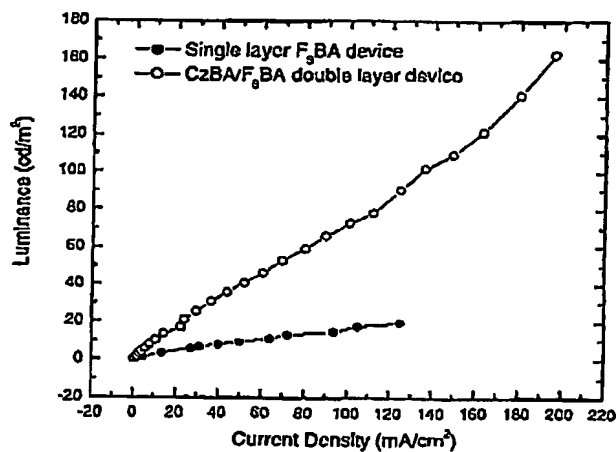


Figure 7

4. The electroluminescence (EL) spectrum of the CzBA/F<sub>3</sub>BA double layer device is identical to the photoluminescence spectrum of F<sub>3</sub>BA thin film (peaked

at 416nm). However, the EL spectrum of a single layer F<sub>3</sub>BA device is very different from the PL of F<sub>3</sub>BA thin film. There is a very broad long-wavelength shoulder appeared in the range of 500-700 nm (Figure 8), that might be caused by imbalanced charge injection (i.e., electrons >> holes) in the device.

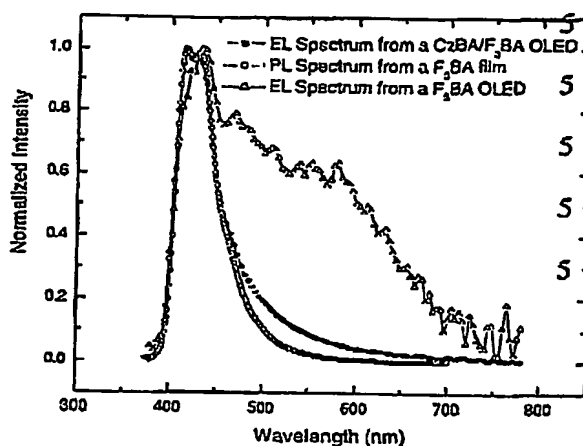


Figure 8

A double layer structure has been fabricated successfully by spin-coating CzBA and F<sub>3</sub>BA solution and the subsequent mild thermal treatment. This demonstrated that the thermal dehydration of diboronic acids to form cross-linked networks could be used as an easy and effective approach to fabricate double or multi-layered devices. Our preliminary experiments on thin film and device processing show that the thin films are quite uniform as indicated by the uniform thickness interference pattern, and uniform light emission area, which depends strongly on the layer thickness. The CzBA layer plays a role of hole-transporting layer, while the F<sub>3</sub>BA layer functions as both an electron-transporting layer and a light-emitting layer. The fact that the fluorescence intensity did not decrease after a thermal treatment at 130 °C indicates the

cross-linking process is useful in enhancing the thermal stability, especially for fluorene-based compounds, which are known spectrally unstable upon heat treatment. The maximum luminance value recorded for the CzBA/F3BA double layer device is around  $170 \text{ cd/m}^2$ . This value is obtained from a luminance meter which is calibrated

5 as a photopic response device (Figure 9).

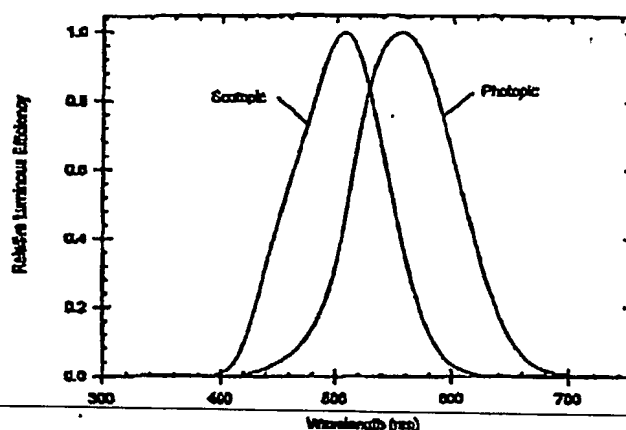


Figure 9 CIE spectral luminous efficiency functions for photopic vision,  $V(\lambda)$ , and scotopic vision,  $V'(\lambda)$ .

The advantage of using boronic acid groups:

Applying dehydration of boronic acids to fabricate multi-layered thin films has several advantages:

- I. Processability by conventional spin-coating technology and very mild cross-linking conditions (room temperature –  $130^\circ\text{C}$  under vacuum) allow cost-effective fabrication of thin films.

II. The crosslinking reactions do not require any initiators and can be carried out under quite low temperatures (as low as room temperature) with water as the only by-product that can be easily removed under vacuum. Therefore there is no generation of highly reactive radicals involved and no harmful initiator residues left in the materials.

5

III. Multi-layered device structure can be easily realized using materials containing organoboronic acid groups. We have demonstrated that a CzBA layer and an F3BA layer can be stacked on each other forming double layer structure; the total thickness of the double layer structure equals to the sum of the two individual layers. Figures 5-7 illustrates that we have incorporated desired hole-transporting, electron-transporting and emissive properties into a double layer devices using CzBA and F3BA, and each layer functioned as designed.

10

IV. Because each layer is cross-linked before applying the next layer, this technique can be applied to multi-layer structure or "super-lattice" type structure, not like the solubility based technique that only allows very limited layers.

15

V. High purity and mono-disperse chromophores give uniform optical and electronic properties and minimise the defects in the devices.

VI. No unstable or harmful terminal groups as in other oligomers or polymers, which could detract from the devices' stability.

20

VII. Thermally stable (organic/inorganic hybrid materials) as indicated in Figures 2 & 3 by comparing the photoluminescent spectrum and intensity before and after a thermal treatment in vacuum at 130 °C for two hours.

5 VIII. Because organic light emitting devices are very sensitive to the charge mobility, HOMO-LUMO level positions, and interface quality, the demonstration of a working OLED device indicate a reasonably good interface structure between the CzBA and F3BA layers. Since OLED is only  
10 used here as a testing vehicle, we expect the same film processing technique (using organoboronic acid groups as end caps) can be applied to the fabrication of photovoltaic cells, photonic multi-layer structures, and other electronic/optical devices,

IX. The properties of each layer are easily tunable by varying functional units in the boronic acid precursor or by simply mixing different precursors. There are very wide selections of functional units for the precursors with different optical and physical properties. On the other hand, the  
15 crosslinking of boronic acid groups could enhance compatibility of different components in the layer, and therefore could improve targeted properties.

20 X. Because of the end group crosslinking of the precursors, the amorphous morphology of the layers can be stabilized. The structure with such high crosslinking density will efficiently prevent any aggregation and crystallization, which is usually found in PLED and OLED devices, and cause the performance of the device to decline.